

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
27 December 2001 (27.12.2001)

PCT

(10) International Publication Number  
**WO 01/97973 A1**

(51) International Patent Classification<sup>7</sup>: **B01J 39/20**, 41/14, 45/00, C03C 25/26, 25/28, 25/30

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(21) International Application Number: PCT/US01/19952

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date: 20 June 2001 (20.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/599,811 21 June 2000 (21.06.2000) US

(71) Applicant: BOARD OF TRUSTEES OF UNIVERSITY OF ILLINOIS [US/US]; 352 Henry Administration Building, 506 S. Wright, Urbana, IL 61801 (US).

(72) Inventors: ECONOMY, James; 105 Whitehall Court, Urbana, IL 61801 (US). DOMINGUEZ, Lourdes; 713 South Walnut, Urbana, IL 61801 (US). BENAK, Kelly; 2901 Heritage Drive, Champaigne, IL 61822 (US).

(74) Agent: RAUCH, Paul, E.; Brinks Hofer Gilson & Lione, P.O. Box 10087, Chicago, IL 60610 (US).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/97973 A1**

(54) Title: POLYMERIC ION EXCHANGE FIBERS

(57) Abstract: Ion exchange resin composite fibers include a substrate fiber, and an ion exchange resin, on the substrate fiber. The ion exchange resin composite fibers exhibit greatly increased kinetic rates of reaction and regeneration.

-1-

TITLE

POLYMERIC ION EXCHANGE FIBERS

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The subject matter of this application was in part funded by the  
5 National Science Foundation (Grant no. DMR-97-12489; UFAS No. 1-5-  
31414). The government may have certain rights in this invention.

BACKGROUND

The present invention relates to ion exchange materials.

Ion exchange materials have been used for purification and  
10 demineralization. These materials have a three-dimensional network to which  
ions are attached. In ion exchange resins, the three-dimensional network is a  
polymer. In carbon ion exchangers, the three-dimensional network is  
activated carbon.

Ion exchange resins have been known for almost sixty years ("Ion  
15 Exchangers"; Dorfner, K. (Ann Arbor Science Publishers, Inc.1972)). The  
three-dimensional network helps preserve the structural integrity of the  
material, usually in the form of beads, while the ions provide exchange sites.  
A large variety of ion exchange resins are described in "Encyclopedia of  
Chemical Technology" Kirk-Othmer, 3rd ed., vol. 13, pp. 685-93 (1981); and  
20 "Ion Exchangers" ed. Konrad Dorfner, pp. 28-44, and pp. 206-84 (Walter de  
Gruyter, 1991).

These materials suffer from a number of disadvantages. During the  
activation of the resin (the stage of attachment of the ions), solvent must be  
used to pre-swell the cross-linked resin, to reduce the effects of osmotic  
25 shock. Furthermore, the beads are very susceptible to fracture and breakage  
and must be kept wet at all times. Also, pre-swelling prior to service is often  
required, increasing shipping costs. Finally, there is also a need for ion  
exchange resins having higher contact efficiencies, speed of regeneration,  
and longer service life.

-2-

Glass or mineral fibers, coated with activated carbon, have been prepared. These materials are described in U.S. patent no. 5,834,114. Glass or mineral fibers coated with activated carbon are described as being prepared by coating a glass or mineral fiber substrate with a resin, cross-linking the resin, heating the coated fiber substrate and resin to carbonize the resin, and exposing the coated fiber substrate to an etchant to activate the coated fiber substrate.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the capacities resulting from varied sulfonation treatments of samples and comparative samples; and

Figure 2 is a graph showing batch rates of exchange at varying saline concentrations of samples and comparative samples.

## BRIEF SUMMARY

In a first aspect, the present invention includes a composite, containing (i) a substrate fiber, and (ii) an ion exchange resin, on the substrate fiber.

In a second aspect, the present invention includes a method of making a composite, including forming an ion exchange resin from a resin. The resin is on a substrate fiber.

The term "ion exchange resin" means a resin that contains an ionic group, thus allowing the material to exchange ions with a solvent, but also means a resin that contains groups capable of chelating ions.

## DETAILED DESCRIPTION

The ion exchange resin composite fibers exhibit greatly increased kinetic rates of reaction and regeneration, as compared with commercially available ion exchange resins in the form of beads. Furthermore, the strength is increased by the substrate fiber, reducing fracture and breakage, and allowing a larger variety of forms to be produced. In addition, the thickness of the ion exchange resin on the composite may be very thin, providing excellent kinetics, and preferably the need for solvents for activation or prior to end-use

-3-

may be eliminated, while thicker coatings may provide much higher capacities.

The substrate fiber may include any material that can tolerate the conditions necessary to form the structure. Examples include natural fibers, HEPA filters, e-glass fibers, synthetic fibers used in clothing, polyesters, polyethylene, polyethylene terephthalate, nylon 6, nylon 66, polypropylene, KEVLAR™, liquid crystalline polyesters, and syndiotactic polystyrene. Other examples include natural and synthetic fibers, for example: glass fibers; mineral fibers such as asbestos and basalt; ceramic fibers such as TiO<sub>2</sub>, SiC, and BN; metal fibers such as iron, nickel and platinum; polymer fibers such as TYVEK™; natural fibers such as cellulose and animal hair; and combinations thereof. Some preferred substrate fibers are listed in the table below.

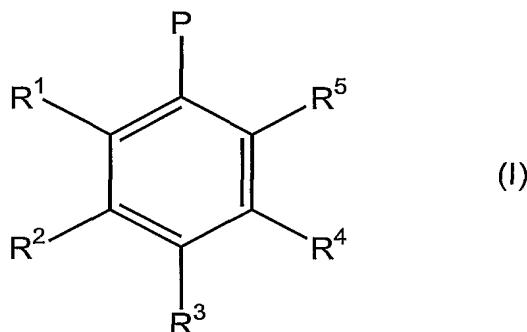
Company	Product Line	Description
CRANE & CO.	Crane 230 (6.5μm) Crane 232 (7.5μm)	Non-woven Fiber Glass Mats Non-woven Fiber Glass Mats
FIBRE GLAST	519 (0.75 oz.) 573 (9 oz.)	wovens wovens
HOLLINGSWORTH & VOSE	BG05095 HE1021	glass paper or felts
JOHNS MANVILLE	DURAGLASS ® 7529 (11μm)	non-woven fiber glass mats
LYDALL MANNING	MANNIGLAS®	non-woven fiber glass mats
DUPONT	TYVEK®	HDPE Spun bonded paper

The ion exchange resin composite fibers may be present in any form. Examples include loose fibers, woven and non-woven fabrics, papers, felts and mats. The ion exchange resin composite fibers may be made from substrate fibers already present in a specific form, or the ion exchange resin composite fibers may first be prepared from loose substrate fibers, and made into the specific form. Furthermore, the ionic exchange resin may itself be used as an adhesive to hold the fibers together.

Any ion exchange resin may be used in the ion exchange resin composite fibers. A large variety of ion exchange resins are described in "Encyclopedia of Chemical Technology" Kirk-Othmer, 3rd ed., vol. 13, pp.

-4-

685-93 (1981); and "Ion Exchangers" ed. Konrad Dorfner, pp. 28-44, and pp. 206-84 (Walter de Gruyter, 1991), both of which are hereby incorporated by reference. Examples include polystyrenes such as polystyrene cross-linked with divinylbenzene, copolymers of methacrylate and styrene cross-linked with divinylbenzene, each also containing ionic or chelating groups; polyvinylpyridines; and poly(meth)acrylic acids such as polymethacrylic acid cross-linked with divinylbenzene, which may contain additional ionic or chelating groups. Preferably, the resin is a cross-linked polymer comprising phenyl groups, for example a polymer containing groups of the formula (I):



where P indicates where the group of formula (I) is attached to the polymer, and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> are each independently selected from H, halo, C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>1</sub>-C<sub>10</sub> haloalkyl, C<sub>1</sub>-C<sub>10</sub> alkenyl, an ionic group and a chelating group, where at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> is an ionic group or a chelating group.

Examples of ionic groups are anionic groups such as -SO<sub>3</sub><sup>-</sup>, -COO<sup>-</sup>, -PO<sub>3</sub><sup>-</sup> and AsO<sub>3</sub>(H)<sup>-</sup>; and cationic groups such as trialkyl ammonium groups, -(R<sup>1</sup>)<sub>3</sub>N<sup>+</sup>, where each R<sup>1</sup> is independently an alkyl group (i.e. methyl, ethyl, propyl, butyl, etc.). Examples of chelating groups include hydroxyl, amino, iminodiacetate groups and thiol groups. Mixtures of different anionic groups, or cationic groups, or chelating groups are possible, as well as mixtures of anionic, cationic and/or chelating groups.

The length of the ion exchange resin composite fibers are not limited, and may be, for example, 0.01 mm to 100 m in length. The ion exchange resin composite fibers may be prepared from longer substrate fibers, then cut or chopped. Furthermore, the diameter of the ion exchange resin composite

-5-

fibers are also not limited, and may be, for example 100 Å to 1 mm in diameter. Preferably, the fibers have an aspect ratio of at least 10.

The ion exchange resin of the ion exchange resin composite fibers may be present on isolated regions on the surface of the substrate fibers, may completely enclose the substrate fibers, or enclose all of the substrate fibers except the ends of the substrate fibers. For example, if the substrate fibers were completely enclosed by the ion exchange resin, then chopping would result in the ends of the fibers being exposed.

The weight ratio between the ion exchange resin and the substrate fibers in the ion exchange resin composite fibers is not limited, but does affect final properties. For example, if the amount of ion exchange resin is very large compared to the amount of substrate fibers, then the brittleness of the ion exchange resin may reduce the flexibility of the ion exchange resin composite fibers. Preferably, the ion exchange resin composite fibers include 10 to 90% by weight of ion exchange resin, more preferably 20 to 80% by weight of ion exchange resin, including 30%, 40%, 50%, 60%, and 70% by weight of ion exchange resin.

The ion exchange resin composite fibers may be prepared by coating the substrate fibers with a resin, and then converting the resin into an ion exchange resin, by introducing ionic and/or chelating groups by chemical reaction with modifying agents. Examples of resins include polystyrenes such as polystyrene cross-linked with divinylbenzene and copolymers of methacrylate and styrene cross-linked with divinylbenzene; poly (vinylbenzyl halides) such as poly (vinylbenzyl chloride) cross-linked with divinylbenzene; and poly(meth)acrylates such as polymethacrylate cross-linked with divinylbenzene. The resin may contain phenyl groups.

One method to coat the resin on the substrate fibers is to start the formation of the resin by polymerizing monomers, stop the polymerization before the polymerizing mixture becomes a gel, coat the fibers with the mixture, and then complete the polymerization. The viscosity of the polymerizing mixture can be adjusted with a solvent, so that the thickness of the coating on the fibers can be easily controlled.

-6-

In a second method, a first polymer can be formed, which is then dissolved into a solvent. Optionally, a cross-linking agent could be added to this mixture. The mixture is coated onto the fibers, and then the solvent is removed. The polymer is then cross-linked, for example by exposure to a cross-linking agent, by exposure to radiation, or activation of the optionally added cross-linking agent. The coated fibers, either before or after cross-linking, may be made into a different form, such as a mat, using the resin as an adhesive to hold the coated fibers together, for example by pressing the coated fibers together while heating.

In a third method, a resin is melted, and the melt is coated onto the fibers. Optionally, the resin may be exposed to a cross-linking agent, or exposed to radiation. Furthermore, the coated fibers may be made into a different form, such as a mat, using the resin as an adhesive to hold the coated fibers together, for example by pressing the coated fibers together while heating.

Any method may be used to coat the fibers, including dip coating and spray coating.

An activating agent is used to form ionic or chelating groups in the resin, to form the ion exchange resin. The selection of activating agent depends on the group in the resin where the ionic group or chelating group will be formed, as well as which ionic or chelating group is desired. In the case of polystyrene, the ionic groups may be attached to phenyl groups in the polymer, such as by reaction with sulfuric acid (to attach sulfonyl groups) or in the case of poly(vinylbenzyl chloride), with trimethyl amine (to attach trialkyl ammonium groups). In the case of poly(meth)acrylates, the acid groups may be formed by saponification of the esters, by reaction with an acid. Preferably no solvent is used during the activation process, because swelling caused by the solvent may result in delamination of the resin from the fiber.

-7-

The following examples and preparations are provided merely to further illustrate the invention. The scope of the invention is not construed as merely consisting of the following examples.

5

Example 1. Polymerization and activation of cationic resin coated glass fibers

I. Polymerization:

10 A copolymer of styrene, 8% wt. divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene), and benzoyl peroxide initiator, were rigorously mixed and heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath, to form the oligomer. The fiberglass substrate  
15 CRANE 230 (6.5 µm fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for one hour. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 60 - 65% by weight was achieved.

20

II. Functionalization:

25 The resin-coated fibers were treated with 150-ml concentrated sulfuric acid for four hours at 85°C with 1% silver sulfate as a catalyst under stirring. After activation, the samples were treated to a stepped-dilution rinse (50%, 25%, 12%, 6%, and 3% sulfuric acid rinse). Finally, the resin-coated fibers were rinsed with pure de-ionized water until all excess acid had been removed.

Example 2. Polymerization and activation of cationic resin coated glass fibers

30

I. Polymerization:

Same as Example 1

II. Functionalization:

The resin-coated fibers were treated with 150-ml concentrated sulfuric acid for twelve hours at 25°C with 1% silver sulfate as a catalyst under stirring. After activation, the samples were treated to a stepped-dilution rinse (50%, 25%, 12%, 6%, and 3% sulfuric acid rinse). Finally, the resin-coated fibers were rinsed with pure de-ionized water until all excess acid had been removed.

10 Example 3. Polymerization and activation of cationic resin coated glass fibers

I. Polymerization:

A copolymer of styrene, 5 wt.% divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene), and benzoyl peroxide initiator were rigorously mixed and heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath, to form the oligomer. The fiberglass substrate CRANE 230 (6.5 µm fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for one hour. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 60 - 65% by weight is achieved.

25 II. Functionalization:

Same as Example 1

Example 4. Polymerization and activation of anionic resin coated glass fibers

I. Polymerization:

30 A copolymer of vinylbenzyl chloride, 8 wt.% divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene) were rigorously mixed with benzoyl peroxide initiator and

-9-

heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the gel point, and subsequently quenched in an ice bath. The fiberglass substrate CRANE 230 (6.5 µm fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for four hours. Excess monomer must be removed with a paper towel or other adsorbent. The coated glass samples were cured at 85°C in a Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 80 - 90% by weight is achieved.

5

10

## II. Functionalization:

15

The resin-coated fibers were treated with ~ 50 ml of trimethylamine for 45 minutes at 25°C. After activation, the samples were rinsed with approximately 200 ml of 2N HCl. Finally, the resin-coated fibers were rinsed with pure de-ionized water and placed in a vacuum furnace overnight at 65°C to dry.

Example 5. Polymerization and activation of anionic resin coated glass fibers

20

## I. Polymerization:

Same as Example 1

25

## II. Functionalization:

The resin-coated fibers were treated with ~ 50 ml of trimethylamine for 20 minutes at 45°C. After activation, the samples were rinsed with approximately 200 ml of 2N HCl. Finally, the resin-coated fibers were rinsed with pure de-ionized water and placed in a vacuum furnace overnight at 65°C to dry.

30

Example 6. Polymerization and activation of anionic resin coated glass fibers

## I. Polymerization:

-10-

A copolymer of vinylbenzyl chloride, 5% wt. divinylbenzene (80% mixture of m, p isomers and >17% ethylvinylbenzene, and <1% o, m, p diethylbenzene) were rigorously mixed with benzoyl peroxide initiator and heated at 80 to 85 °C for approximately 17 to 24 minutes, or just before the 5 gel point, and subsequently quenched in an ice bath, to form the oligomer. The fiberglass substrate Crane 230 (6.5 µm fiber diameter) was then coated with the oligomer. The fibers were then turned occasionally to avoid pooling while sitting in air for four hours. Excess monomer was removed with a paper towel or other adsorbent. The coated glass samples were cured at 85°C in a 10 Lindberg furnace under nitrogen for 4 hours. Following this procedure, a resin loading of 80 - 90% by weight is achieved.

## II. Functionalization:

Same as Example 1.

15

### Batch Capacity Experiments

The cation capacity was determined in a conventional manner. In a 150-ml beaker was added 50 ml of 1M sodium chloride solution (excess), < 0.5-g sample of dry resin coated fibers, and two drops of phenolphthalein 20 indicator. The contents were stirred and titrated with standard 0.1-M sodium hydroxide solution. The volume of sodium hydroxide used, times the normality per gram of exchange material, is representative of the normalized loading capacity in meq/g units. The results are shown Figure 1. The samples were prepared in the same was as Example 1, except that the time 25 of sulfonation and/or temperature of sulfonation was varied as indicated in the figure.

### Regeneration Studies

After each capacity run, samples were regenerated with a solution of 30 2N HCl acid, rinsed thoroughly with deionized water and thoroughly dried overnight. After each cycle, samples were weighed directly after drying to keep water adsorption to a minimum for capacity measurements. These

-11-

systems were successfully regenerated for up to ten times with little to no observable weight loss or loss in activity.

#### Kinetics Studies

5       Batch kinetic tests for the polymeric coated glass fibers of Examples 1 were conducted with saline solutions of varying concentrations (0.01M and 0.005 M NaCl). The samples were vacuum dried at 62°C. After weighing, the resin coated fibers were tested bone dry. Exactly 50 ml of 0.05-M sodium chloride solution was placed in a 150-ml beaker with two drops of phenolphthalein indicator, and 1ml of standard sodium hydroxide. While stirring, a known mass of dry resin-coated fabric was added and the time required to discharge the indicator (neutralize the solution) was noted. This step was repeated until the indicator no longer discharged. The comparative polymeric beads were from Purolite - Type C-150H. The results are shown in  
10      Figure 2.

15      Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.  
20

-12-

## CLAIMS

1. A composite, comprising:

(i) substrate fibers, and

(ii) an ion exchange resin, on said substrate fibers.

5 2. The composite of Claim 1, wherein said ion exchange resin comprises phenyl groups.

3. The composite of Claim 1, wherein said substrate fibers comprises a member selected from the group consisting of glass, polymer, and mixtures thereof.

10 4. The composite of Claim 1, wherein said ion exchange resin comprises ionic groups.

5. The composite of Claim 1, wherein said ion exchange resin comprises chelating groups.

15 6. The composite of Claim 1, wherein said substrate fibers are in the form of one member selected from the group consisting of fabrics, papers, felts and mats.

7. The composite of Claim 4, wherein said ionic groups are selected from the group consisting of sulfonic groups and trialkyl ammonium groups.

20 8. The composite of Claim 4, wherein said ion exchange resin comprises polystyrene cross-linked with divinylbenzene.

9. The composite of Claim 8, wherein said substrate fibers comprise glass.

25 10. A method of making a composite, comprising:

forming an ion exchange resin from a resin;  
wherein said resin is on substrate fibers.

-13-

11. The method of Claim 10, further comprising, prior to said forming, coating said resin on said substrate fibers.

12. The method of Claim 10, wherein said forming comprises reacting said resin with an activating agent.

5 13. The method of Claim 12, wherein said resin comprises phenyl groups.

14. The method of Claim 13, wherein said activating agent is selected from the group consisting of sulfuric acid and trimethyl amine.

10 15. The method of Claim 10, wherein said substrate fibers comprise a member selected from the group consisting of glass, polymer, and mixtures thereof.

16. The method of Claim 10, wherein said substrate fibers are in the form of one member selected from the group consisting of fabrics, papers, felts and mats.

15 17. The method of Claim 10, wherein said resin comprises polystyrene cross-linked with divinylbenzene.

18. The method of Claim 17, wherein said substrate fibers comprise glass.

20 19. The method of Claim 18, wherein said forming comprises reacting said resin with an activating agent selected from the group consisting of sulfuric acid and trimethyl amine.

20. A composite, prepared by the method of Claim 10.

21. A composite, prepared by the method of Claim 12.

22. A composite, prepared by the method of Claim 14.

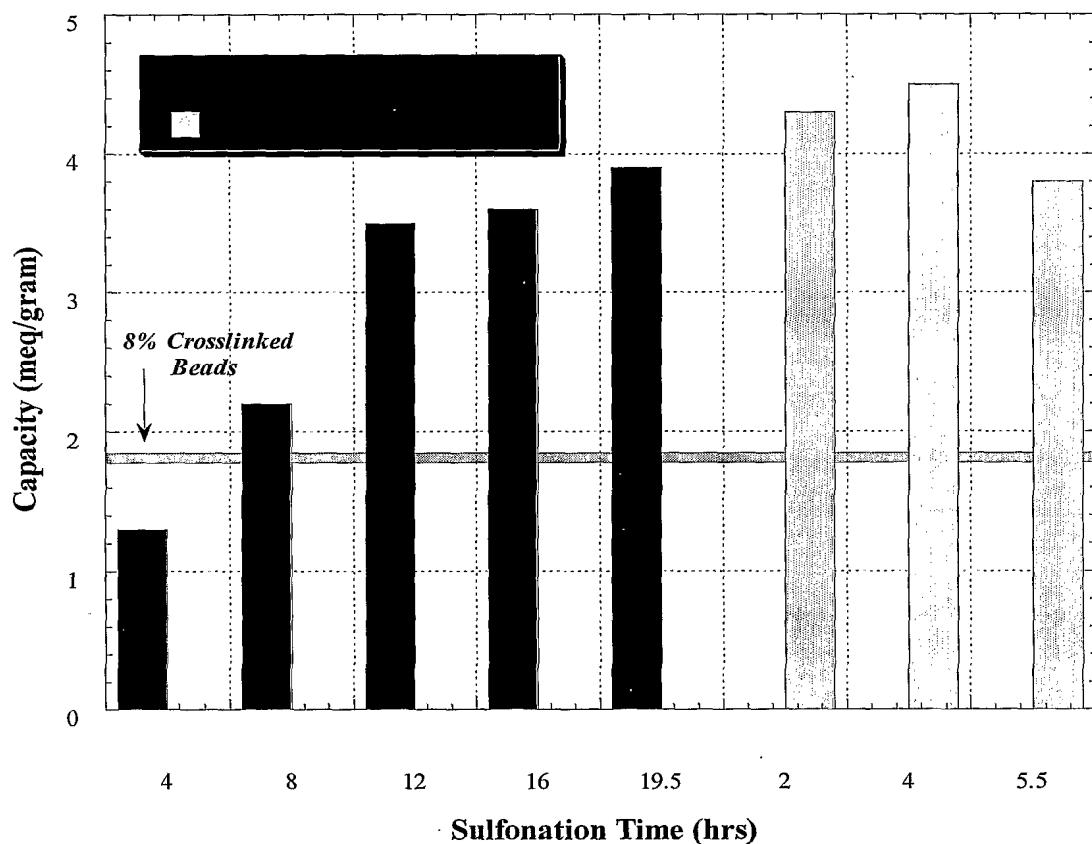
25 23. A composite, prepared by the method of Claim 17.

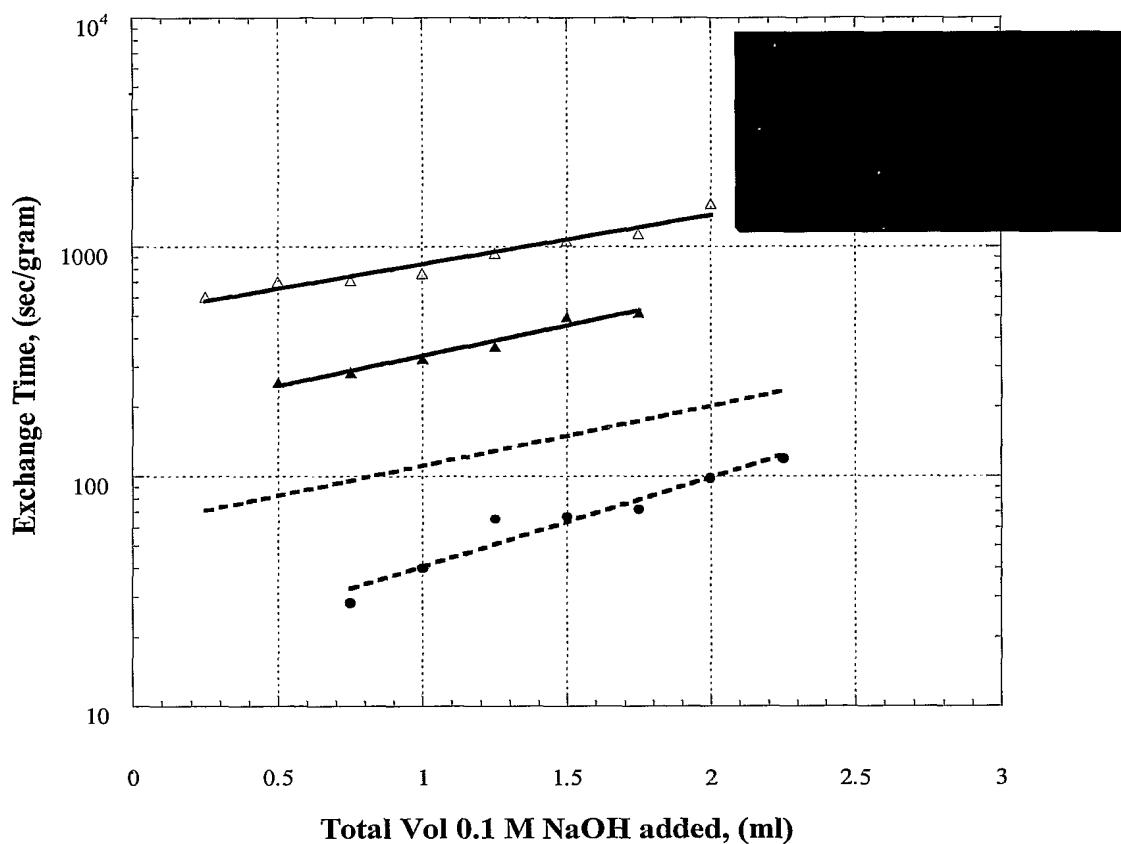
-14-

24. A composite, prepared by the method of Claim 18.
25. A composite, prepared by the method of Claim 19.
26. A method of purifying a liquid, comprising:  
contacting a liquid with the composite of Claim 1.
- 5 27. A method of purifying a liquid, comprising:  
contacting a liquid with the composite of Claim 6.
28. A method of purifying a liquid, comprising:  
contacting a liquid with the composite of Claim 20.

10

15

**Figure 1: Capacities Resulting from Varied Sulfonation Treatments**

**Figure 2: Batch Rates of Exchange at Varying Saline Concentration**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/19952

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 B01J39/20 B01J41/14 B01J45/00 C03C25/26 C03C25/28  
C03C25/30

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01J C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 318 846 A (BRUENING RONALD L ET AL) 7 June 1994 (1994-06-07) the whole document ---	1-28
Y	EP 0 630 685 A (INST TEXTILE DE FRANCE) 28 December 1994 (1994-12-28) claims ---	1-4,6-28
Y	US 5 350 523 A (TOMOI MASAO ET AL) 27 September 1994 (1994-09-27) claims ---	1-4,6-28
Y	EP 0 036 584 A (RIEDEL DE HAEN AG) 30 September 1981 (1981-09-30)  page 1, line 1 -page 5, last paragraph ---	1,5, 10-13, 15-21, 23-28  -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

7 November 2001

Date of mailing of the international search report

14/11/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Reedijk, A

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/19952

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 547 760 A (TARBET BRYON J ET AL) 20 August 1996 (1996-08-20)  column 2, line 6 -column 3, line 38 ---	1,5, 10-13, 15-21, 23-28
A	EP 0 045 824 A (TOKYO ORGAN CHEM IND) 17 February 1982 (1982-02-17) the whole document -----	1-28

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 01/19952

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5318846	A	07-06-1994	US US AT AU AU BR CA CN CN DE DE EP ES FI HU JP MX NO PL RU WO ZA	5190661 A 5446182 A 175133 T 661917 B2 4530593 A 9306504 A 2136635 A1 1090794 A ,B 1152477 A 69322864 D1 69322864 T2 0644799 A1 2128430 T3 945746 A 69074 A2 8500766 T 9303429 A1 944702 A 171797 B1 2116828 C1 9325306 A1 9304034 A	02-03-1993 29-08-1995 15-01-1999 10-08-1995 04-01-1994 15-09-1998 23-12-1993 17-08-1994 25-06-1997 11-02-1999 27-05-1999 29-03-1995 16-05-1999 07-12-1994 28-08-1995 30-01-1996 01-12-1993 06-12-1994 30-06-1997 10-08-1998 23-12-1993 06-01-1994
EP 0630685	A	28-12-1994	FR AT CA DE DE EP ES	2708273 A1 176875 T 2126584 A1 69416618 D1 69416618 T2 0630685 A1 2131180 T3	03-02-1995 15-03-1999 29-12-1994 01-04-1999 09-09-1999 28-12-1994 16-07-1999
US 5350523	A	27-09-1994	JP JP JP JP DE DE EP JP	3147389 B2 4349941 A 3147945 B2 5057200 A 69119268 D1 69119268 T2 0444643 A2 2001089523 A	19-03-2001 04-12-1992 19-03-2001 09-03-1993 13-06-1996 31-10-1996 04-09-1991 03-04-2001
EP 0036584	A	30-09-1981	DE EP JP	3011393 A1 0036584 A2 57007262 A	01-10-1981 30-09-1981 14-01-1982
US 5547760	A	20-08-1996	AU AU BR CA CN CZ EP FI HU JP JP LT LV NO	686796 B2 2295295 A 9507546 A 2188649 A1 1151128 A 9603097 A3 0757589 A1 964305 A 75287 A2 3100638 B2 9511948 T 96152 A ,B 11791 A 964536 A	12-02-1998 16-11-1995 05-08-1997 02-11-1995 04-06-1997 17-09-1997 12-02-1997 23-12-1996 28-05-1997 16-10-2000 02-12-1997 26-05-1997 20-06-1997 25-10-1996

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/19952

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
US 5547760	A		NZ 284360 A	26-01-1998
			PL 317023 A1	03-03-1997
			WO 9529008 A1	02-11-1995
			US 5618433 A	08-04-1997
			US 5980987 A	09-11-1999
			US 2001021413 A1	13-09-2001
EP 0045824	A	17-02-1982	EP 0045824 A1	17-02-1982